

Appendix D

Methodology for Estimating Nickel Emissions from Thermal Spraying

D.1. Introduction

Estimating air emissions can be accomplished by direct measurement of facility exhaust gases or by performing calculations based on material usage. Measurement of exhaust gases is generally the preferred method for individual facilities, but conducting stack exhaust tests can be costly. Therefore, we have developed calculation methods that can be used to estimate nickel emissions for different types of thermal spraying processes and the associated air pollution control devices. The following sections describe the process that was used to develop emission estimation methods for thermal spraying.

D.2. Nickel Emission Factors - Summary

The general approach for estimating nickel emissions involves multiplying emission factors by usage rates. Emission factors were obtained from a variety of sources, based on the type of process and control device. In some cases, emission factors were taken directly from stack test results, while other factors were derived from a combination of stack test results and data on control efficiencies. Table D-1 summarizes the emission factors that were used and Section D.3 describes how these factors were derived.

Table D-1:
Emission Factor Summary – Nickel

Process	Emission Factors (lbs Ni/lb Ni sprayed)			
	0% Ctl. Eff. (Uncontrolled)	90% Ctl. Eff. ¹ (e.g. Water Curtain)	99% Ctl. Eff. (e.g. Dry Filter)	99.97% Ctl. Eff. (e.g., HEPA Filter)
Twin-Wire Electric Arc Spray ²	6.0E-03	6.0E-04	6.0E-05	1.8E-06
Flame Spray ³	1.10E-01	4.64E-02	1.10E-03	3.30E-05
HVOF ³	1.10E-01	4.64E-02	1.10E-03	3.30E-05
Plasma Spray ⁴	1.5E-01	3.67E-02	1.5E-03	1.72E-05
Other Thermal Spraying ⁵	9.4E-02	3.25E-02	9.4E-04	2.13E-05

1. Listed below the control efficiencies are examples of control devices that may meet the control efficiency.

2. Uncontrolled emission factor based on Wisconsin stack test data.

3. Emission factors based on SDAPCD stack test data for flame spraying.

4. Emission factors based on SCAQMD and SDAPCD stack test data.

5. For "Other Thermal Spraying" processes, we used an average of the emission factors for the listed thermal spraying processes.

D.3. Nickel Emission Factor Development

The following sections describe how emission factors were derived from various sources for different types of thermal spraying processes and control devices. In each case, emission factors were developed for operations that had no air pollution control devices (i.e., uncontrolled) and for operations that had control devices (i.e., controlled).

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To determine controlled emission factors in the absence of stack test data, we used the following equation:

$$\text{Eqn. D.1: } [\text{Controlled Emission Factor}] = [\text{Uncontrolled Emission Factor}] * [1 - \text{Control Efficiency}]$$

Controlled emission factors were developed for the following levels of control:

Control Efficiency Levels

90%	(e.g., a water curtain)
99%	(e.g., a dry filter)
99.97%	(e.g., a HEPA filter)

The actual control efficiency for a control device at a particular facility can depend on specific parameters (e.g., particle size, filter media, etc.), but the control efficiencies listed above are consistent with general industry estimates.

D.3.2. SDAPCD Emission Factors for Plasma Spraying & Flame Spraying

The San Diego County Air Pollution Control District (SDAPCD) has compiled the following emission factors for various plasma spraying and flame spraying facilities, based on stack test data (SDAPCD, 1998.)

Table D-3:

SDAPCD Emission Factors – Nickel

SDAPCD Method #	Process	Control Device	Emission Factor (lb Ni/lb Ni sprayed)	Average (lb Ni/lb Ni sprayed)
M01	Plasma Spray	HEPA	3.73E-06	1.31E-05
M02	Plasma Spray	HEPA	2.24E-05	
M03	Plasma Spray	HEPA	1.31E-05	
M04	Plasma Spray	Water Curtain	8.10E-04	1.84E-02
M05	Plasma Spray	Water Curtain	3.59E-02	
M06	Plasma Spray	Water Curtain	1.84E-02	
M08	Flame Spray	HEPA	3.30E-05	
M09	Flame Spray	Water Curtain	4.64E-02	

Bold highlighting indicates a value that appears in the emission factor summary table.

The emission factors in Table D-3 are based on stack test data from several thermal spraying facilities in the San Diego area. In addition to these tests, SDAPCD provided results from another stack test that was conducted in 2002 at a plasma spraying facility that was equipped with a HEPA filter. The emission factor from this test was 2.12E-05 lb Ni/lb Ni sprayed (SDAPCD, 2002a). The average emission factor for a plasma spraying facility with a HEPA filter was calculated as shown below:

$$[1.31\text{E-}05 + 2.12\text{E-}05]/2 = \mathbf{1.72\text{E-}05} \text{ lb Ni/lb Ni sprayed}$$

To determine an uncontrolled emission factor for a flame spraying facility, we used the following equation:

$$\text{Eqn. D.3: [Uncontrolled Emission Factor]} = [\text{Controlled Emission Factor}] / [1 - \text{Control Efficiency}]$$

The uncontrolled emission factor for flame spraying was calculated as shown below:

Emission Factor for Flame Spraying with a HEPA Filter = 3.30E-05 lb Ni/lb Ni sprayed

Estimated Control Efficiency for a HEPA Filter = 99.97%

[Uncontrolled Emission Factor] = [3.30E-05] / [1 – 0.9997] = **1.10E-01** lb Ni/lb Ni sprayed

The emission factor for flame spraying with a control device that achieves 99% control efficiency was calculated as shown below:

Uncontrolled Emission Factor for Flame Spraying = 1.10E-01 lb Ni/lb Ni sprayed

Control Efficiency = 99% (e.g., a dry filter)

[Controlled Emission Factor @ 99%] = [1.10E-01] * [1 – 0.99] = **1.10E-03** lb Ni/lb Ni sprayed

The emission factors for flame spraying were also used to estimate emissions from HVOF processes, because they are both combustion-based operations that achieve comparable temperatures.

D.3.3. SCAQMD Emission Factors for Plasma Spraying

The South Coast Air Quality Management District (SCAQMD) worked with Pacific Environmental Services to develop an emission inventory for metal welding, cutting, and spraying operations. In May 2000, Pacific Environmental Services completed an emission inventory report which contained metal spraying emission factors for nickel (PES, 2000). The emission factors for nickel were based on stack tests that were conducted at two facilities in the SCAQMD in 1987 to 1990. Both of the facilities conducted plasma spraying during the stack tests. Table D-4 lists the nickel emission factors from this study.

Table D-4:

Emission Factors - SCAQMD Plasma Spraying

Control Devices	Emission Factors (lb Ni/lb Ni sprayed)
Uncontrolled	1.5E-01
Water Curtain	5.5E-02

Bold highlighting indicates a value that appears in the emission factor summary table.

The emission factor for plasma spraying with a control device that achieves 99% control efficiency was calculated as shown below:

Uncontrolled Emission Factor for Plasma Spraying = 1.5E-01 lb Ni/lb Ni sprayed

Control Efficiency = 99% (e.g., a dry filter)

[Controlled Emission Factor @ 99%] = [1.5E-01] * [1 – 0.99] = **1.5E-03** lb Ni/lb Ni sprayed

Both SDAPCD and SCAQMD provided emission factors for plasma spraying processes with water curtains. We used the average of these two values for our emission factor:

SDAPCD: 1.84E-02 lb Ni/lb Ni sprayed

SCAQMD: 5.5E-02 lb Ni/lb Ni sprayed

Average: $(1.84\text{E-}02 + 5.5\text{E-}02)/2 = \mathbf{3.67\text{E-}02}$ lb Ni/lb Ni sprayed

D.3.4. Wisconsin Data – Twin-Wire Electric Arc Spraying

ARB staff contacted regulatory agencies in other states to gather information on their methods for estimating emissions from thermal spraying sources. Wisconsin staff provided nickel emissions data for a facility that conducted electric arc spraying. The facility used nickel-based materials that do not contain chromium. Emissions were controlled by a baghouse and a HEPA filter. Based on stack test results, the control efficiency was 99.9% and the nickel emission factor was 6.0E-06 lbs Ni/lb Ni sprayed. The average spray rate during the stack testing was 31 lbs Ni/hr.

To determine an uncontrolled emission factor for a twin-wire electric arc spraying process, we used the following equation:

$$\text{Eqn. D.4: } [\text{Uncontrolled Emission Factor}] = [\text{Controlled Emission Factor}] / [1 - \text{Control Efficiency}]$$

The uncontrolled emission factor for twin-wire electric arc spraying was calculated as shown below:

Emission Factor for Twin-Wire Electric Arc Spraying = 6.0E-06 lb Ni/lb Ni sprayed

Control Efficiency, based on Wisconsin stack test data for this facility = 99.9%

[Uncontrolled Emission Factor] = $[6.0\text{E-}06] / [1 - 0.999] = \mathbf{6.0\text{E-}03}$ lb Ni/lb Ni sprayed

The emission factor for twin-wire electric arc spraying with a control device that achieves 90% control efficiency was calculated as shown below:

Uncontrolled Emission Factor for Twin-Wire Electric Arc Spraying = 6.0E-03 lb Ni/lb Ni sprayed

Control Efficiency = 90% (e.g., a water curtain)

[Controlled Emission Factor @ 90%] = $[6.0\text{E-}03] * [1 - 0.9] = \mathbf{6.0\text{E-}04}$ lb Ni/lb Ni sprayed

The emission factor for twin-wire electric arc spraying with a control device that achieves 99% control efficiency was calculated as shown below:

Uncontrolled Emission Factor for Twin-Wire Electric Arc Spraying = 6.0E-03 lb Ni/lb Ni sprayed

Control Efficiency = 99% (e.g., a dry filter)

[Controlled Emission Factor @ 99%] = $[6.0\text{E-}03] * [1 - 0.99] = \mathbf{6.0\text{E-}05}$ lb Ni/lb Ni sprayed

The emission factor for twin-wire electric arc spraying with a control device that achieves 99.97% control efficiency was calculated as shown below:

Uncontrolled Emission Factor for Twin-Wire Electric Arc Spraying = 6.0E-03 lb Ni/lb Ni sprayed

Control Efficiency = 99.97% (e.g., a HEPA filter)

[Controlled Emission Factor @ 99.97%] = $[6.0\text{E-}03] * [1 - 0.9997] = \mathbf{1.8\text{E-}06}$ lb Ni/lb Ni sprayed

D.4. Emission Calculations - Annual

This section describes how emission factors were used to estimate annual nickel emissions from thermal spraying processes. The general approach involved multiplying emission factors by annual usage rates, as shown in the following equation:

$$\text{Eqn. D.5: } [Emissions, \text{ lbs Ni/year}] = [Emission Factor, \text{ lbs Ni/lb Ni sprayed}] * [Usage, \text{ lbs Ni sprayed/year}]$$

Emission factors were described in Section D.3 and were summarized in Table D-1. Data from the manufacturer survey provided information on the annual material sales quantities and ingredient percentages. We used these data to calculate the amount of nickel in each material and the potential annual usage of nickel, as shown in the following equations:

$$\text{Eqn. D.6: } [Nickel Qty, \frac{\text{lbs}}{\text{yr}}] = [Material Sales, \frac{\text{lbs}}{\text{yr}}] * [Wt\% Nickel]$$

The manufacturer survey also identified the types of thermal spraying processes associated with each product, which allowed us to select the appropriate emission factor. Some thermal spraying materials were designated as being suitable for two types of processes (e.g., flame spray and plasma spray). For these multi-use products, an average emission factor value was used, as shown in the following example calculations:

Average Emission Factor Calculation - Uncontrolled Flame Spray & Plasma Spray:
 $(1.10\text{E-}01 + 1.5\text{E-}01)/2 = 1.3\text{E-}01 \text{ lbs Ni/lb Ni sprayed}$

Example Annual Emissions Calculation - Uncontrolled Flame Spray & Plasma Spray:
 $[10,000 \text{ lbs Ni sprayed}] * [1.3\text{E-}01 \text{ lbs Ni/lb Ni sprayed}] = 1300 \text{ lbs Ni/yr}$

Table D-5 summarizes the California sales in 2002 for thermal spraying products that contain nickel and the associated quantity of nickel contained in those products. Table D-5 also contains the associated processes, emission factors, and emissions values. Potential statewide emissions of nickel vary widely, depending on the type of control device used. For example, if all facilities used control devices with 99.97% control efficiency (e.g., HEPA filters), statewide emissions would be only 1 lb/yr. However, statewide emissions would be more than 4,700 lbs/yr, if all facilities were uncontrolled. Therefore, it is important to identify a control effectiveness when estimating actual statewide emissions. ARB's 2004 Thermal Spraying Facility Survey provided information on the percentage of facilities that use control devices and the types of devices that were used. The results of this survey indicate that 87% of the thermal spraying facilities in California that use materials containing nickel have a control device and the most common type of device is the dry filter cartridge. Based on this information, the following assumptions were made:

- 87% of the thermal spraying material would be used at controlled facilities with dry filters
- 13% of the thermal spraying material would be used at uncontrolled facilities
- $[Controlled Emissions] = [87\%] * [Sales, \text{ lbs}] * [Emission Factor, \text{ lbs Ni/lb Ni sold}]$

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- [Uncontrolled Emissions] = [13%]*[Sales, lbs]*[Emission Factor, lbs Ni/lb Ni sold]

The survey data indicated that some facilities had HEPA filters (generally more efficient than dry filters) and some facilities had water curtains (usually less efficient than dry filters), so the assumption that controlled facilities used dry filters provides a reasonable representation of the average control efficiencies statewide.

Based on these assumptions, 4 tons of nickel were potentially used at uncontrolled facilities, producing 616 lbs of nickel emissions, and 29 tons of nickel were potentially used at controlled facilities, producing 77 lbs of nickel emissions. Therefore, the estimated statewide nickel emissions from thermal spraying are 693 pounds in 2002. Table D-5 provides details of potential material usage emissions for the various thermal spraying processes.

For this thermal spraying ATCM, we estimated the potential emission reductions based on data from the ARB 2004 Thermal Spraying Facility Survey and the proposed ATCM control efficiency requirements. Implementation of this thermal spraying ATCM is expected to reduce nickel emissions by 660 lbs/yr, which represents a 95% decrease in nickel emissions from thermal spraying.

WORKSHOP #3 DRAFT – FOR DISCUSSION ONLY. DO NOT CITE OR QUOTE**Table D-5:*****Thermal Spraying Sales & Emissions Summary***

Process	Material	Sales of Products Containing Nickel (lbs) ¹	Qty. of Nickel (lbs Ni)	0% Control Efficiency			99% Control Efficiency		
				Emission Factor (lbs Ni/lb Ni)	Usage % ²	Emissions (lbs Ni)	Emission Factor (lbs Ni/lb Ni)	Usage % ²	Emissions (lbs Ni)
Flame Spray	Powder	9,917	7,021.1	1.10E-01	13%	100.4	1.10E-03	87%	6.7
Flame Spray/Other	Powder	PD	8,429.3	1.02E-01	13%	111.8	5.85E-03	87%	42.9
Flame Spray/Plasma Spray	Powder	PD	9,567.7	1.30E-01	13%	161.7	1.30E-03	87%	10.8
HVOF	Powder	5,776	1,361.3	1.10E-01	13%	19.5	1.10E-03	87%	1.3
HVOF/Flame Spray/Plasma Spray	Powder	PD	828.0	1.23E-01	13%	13.3	1.23E-03	87%	0.9
HVOF/Plasma Spray	Powder	11,473	6,408.4	1.30E-01	13%	108.3	1.30E-03	87%	7.2
Plasma Spray	Powder	9,435	3,056.7	1.50E-01	13%	59.6	1.50E-03	87%	4.0
Plasma Spray/Other	Powder	PD	63.6	1.22E-01	13%	1.0	6.05E-03	87%	0.3
Powder Subtotal =		67,911	36,736			575.5			74.2
Single-Wire Flame Spray	Wire	PD	1,259.4	1.10E-01	13%	18.0	1.10E-03	87%	1.2
Twin-Wire Electric Arc	Wire	PD	29,320.2	6.00E-03	13%	22.9	6.00E-05	87%	1.5
Wire Subtotal =		57,640	30,580			40.9			2.7
GRAND TOTAL =		125,550	67,316			616.4			76.9

1. "PD": Protected data (fewer than three companies reported sales).

2. Assume 13% of products are used at Uncontrolled facilities and 87% of products are used at facilities with a dry filter control device.

D.5. Nickel Emission Calculations –Hourly

When performing health risk assessments, it is necessary to identify the average hourly emissions and the maximum hourly emissions. The average hourly emissions are used when calculating the possible impacts from long-term chronic exposure to nickel, while the maximum hourly emissions are used to calculate impacts from short-term acute exposures to nickel.

Hourly emissions were estimated using the following equations:

$$\text{Eqn. D.7: [Max. Hourly Emissions, lbs Ni/hour]} = [\text{Emission Factor, lbs Ni/lb Ni sprayed}] * [\text{Usage, lbs Ni sprayed/hour}]$$

$$\text{Eqn. D.8: [Annual Avg. Hourly Emissions, lbs Ni/hour]} = \frac{[\text{Annual Emissions, lbs Ni/yr}]}{[250 \text{ days/yr}] * [\text{Daily Operating Hours, e.g., 8 hrs/day}]}$$

These values are converted into units of grams/second for the risk assessment calculations, using the following equation:

$$\text{Eqn. D.9: [Hourly Emissions, g/s]} = \frac{[\text{Hourly Emissions, lb Ni}]}{[\text{hr}]} * \frac{[453.59 \text{ g}]}{[1 \text{ lb}]} * \frac{[1 \text{ hr}]}{[60 \text{ min}]} * \frac{[1 \text{ min}]}{[60 \text{ sec}]}$$

D.5.1. Maximum Hourly Emissions

The maximum hourly emissions depend on the hourly spray rate for a given facility. To estimate maximum hourly emissions, we used emission factors and a range of spray rates (low, medium, and high) to cover a variety of scenarios. For most thermal spraying processes, the hourly spray rates for nickel were 0.5, 5, and 15 lbs/hr (or 0.063, 0.63, and 1.89 g/s), as shown in Table D-6. Twin-Wire Electric Arc spraying can achieve a substantially higher spray rate than flame spraying, according to information from manufacturers and technical literature. Therefore, the “high” estimated spray rate for electric arc spraying was 25 lbs/hr (or 3.15 g/s) instead of 15 lbs/hr (1.89 g/s). Since different products contain different nickel percentages, the amount of material that corresponds to these nickel spray rates will vary according to product. However, it is possible to get an estimated material spray rate, by using the sales-weighted average nickel percentage from the ARB 2003 Thermal Spraying Materials Survey (ARB, 2004), as shown below.

Table D-6:

Thermal Spraying Estimated Hourly Spray Rates

	Nickel Spray Rates, lbs Ni/hr (grams/second)			Material Spray Rates (lbs/hr)*		
	Low	Medium	High	Low	Medium	High
Flame, Plasma, HVOF, Detonation	0.5 (0.063)	5 (0.63)	15 (1.89)	0.9	9.2	27.7
Electric Arc Spraying	0.5 (0.063)	5 (0.63)	25 (3.15)	0.9	9.4	47.1

*Estimated values based on sales-weighted average nickel percentages from the ARB 2003 Thermal Spraying Materials Survey. 54.1% Ni for Powder, 53.1% Ni for Wire.

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These usage levels are consistent with actual facility spray rates. Spray rates were examined for several thermal spraying facilities in the San Diego area and they ranged from 0.2 – 20 lbs/hr for materials that contain nickel.

Maximum hourly emission rates were estimated for uncontrolled facilities (Table D-7) and for facilities equipped with a control device that achieves 99% control efficiency (Table D-8). The maximum hourly values were calculated for low, medium, and high nickel spray rates. For the purposes of risk assessment, these data are presented in units of “grams/second”, rather than units of “lbs/hr”.

Table D-7:***Maximum Hourly Emissions, 0% Control Efficiency – Nickel***

Process	Material	Emission Factor (g Ni/g Ni)	Estimated Emissions (grams Ni/sec)		
			Low Spray Rate @ 0.063 g/s	Medium Spray Rate @ 0.63 g/s	High Spray Rate @ 1.89 g/s
Flame Spray	Powder	1.10E-01	6.93E-03	6.93E-02	2.08E-01
Flame Spray/Other	Powder	1.02E-01	6.43E-03	6.43E-02	1.93E-01
Flame Spray/Plasma Spray	Powder	1.30E-01	8.19E-03	8.19E-02	2.46E-01
HVOF	Powder	1.10E-01	6.93E-03	6.93E-02	2.08E-01
HVOF/Flame Spray/Plasma Spray	Powder	1.23E-01	7.77E-03	7.77E-02	2.33E-01
HVOF/Plasma Spray	Powder	1.30E-01	8.19E-03	8.19E-02	2.46E-01
Plasma Spray	Powder	1.50E-01	9.45E-03	9.45E-02	2.83E-01
Plasma Spray/Other	Powder	1.22E-01	7.69E-03	7.69E-02	2.31E-01
Single-Wire Flame Spray	Wire	1.10E-01	6.93E-03	6.93E-02	2.08E-01
			Low @ 0.063 g/s	Medium @ 0.63 g/s	High @ 3.15 g/s
Twin-Wire Electric Arc	Wire	6.00E-03	3.78E-04	3.78E-03	1.89E-02

Table D-8:***Maximum Hourly Emissions, 99% Control Efficiency – Nickel***

Process	Material	Emission Factor (g Ni/g Ni)	Estimated Emissions (grams Ni/sec)		
			Low Spray Rate @ 0.063 g/s	Medium Spray Rate @ 0.63 g/s	High Spray Rate @ 1.89 g/s
Flame Spray	Powder	1.10E-03	6.93E-05	6.93E-04	2.08E-03
Flame Spray/Other	Powder	5.85E-03	3.69E-04	3.69E-03	1.11E-02
Flame Spray/Plasma Spray	Powder	1.30E-03	8.19E-05	8.19E-04	2.46E-03
HVOF	Powder	1.10E-03	6.93E-05	6.93E-04	2.08E-03
HVOF/Flame Spray/Plasma Spray	Powder	1.23E-03	7.77E-05	7.77E-04	2.33E-03
HVOF/Plasma Spray	Powder	1.30E-03	8.19E-05	8.19E-04	2.46E-03
Plasma Spray	Powder	1.50E-03	9.45E-05	9.45E-04	2.83E-03
Plasma Spray/Other	Powder	6.05E-03	3.81E-04	3.81E-03	1.14E-02
Single-Wire Flame Spray	Wire	1.10E-03	6.93E-05	6.93E-04	2.08E-03
			Low @ 0.063 g/s	Medium @ 0.63 g/s	High @ 3.15 g/s
Twin-Wire Electric Arc	Wire	6.00E-05	3.78E-06	3.78E-05	1.89E-04

D.5.2. Annual Average Hourly Emissions

Annual average hourly emissions vary, depending on individual facility operating schedules. However, we can estimate the statewide average hourly emissions, based on the total annual emissions statewide. According to the ARB 2004 Thermal Spraying Facility Survey, 30 facilities reported the use of materials that contain nickel.

$$[\text{Annual Avg. Hourly Emissions}] = \frac{[693 \text{ lbs Ni/yr}]}{[250 \text{ days/yr}] * [8 \text{ hrs/day}] * [30 \text{ facilities statewide}]} = \frac{1.16\text{E-}02 \text{ lbs Ni}}{\text{hr}}$$

$$[\text{Hourly Emissions, g/s}] = \frac{[1.16\text{E-}02 \text{ lbs Ni}]}{[\text{hr}]} * \frac{[453.59 \text{ g}]}{[1 \text{ lb}]} * \frac{[1 \text{ hr}]}{[60 \text{ min}]} * \frac{[1 \text{ min}]}{[60 \text{ sec}]} = \frac{1.46\text{E-}03 \text{ g Ni}}{\text{sec}}$$

This statewide average is at the high end of values that are based on individual facility data, as reported in the 2004 ARB Thermal Spraying Facility Survey. For most facilities that reported nickel usage, the annual average emissions were generally between 7E-08 g/s – 3E-03 g/s, with one outlier that exceeded 3E-02 g/s. Since the total sales reported by manufacturers were greater than the total usage reported by individual facilities, it is not surprising that annual average emissions based on manufacturer sales would be higher than emissions based on individual facility data.

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